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Procedia Engineering 32 (2012) 909 – 915

Procedia Engineering

www.elsevier.com/locate/procedia

I-SEEC2011

Raman Characterization and Mechanical Properties of the Silicon Nitride/Diamond-Like Carbon Composites Film Prepared by Co-Deposition of RF Magnetron and Filter Cathodic Arc

P. Bunnak[a,b*] and P. Limsuwan[a,c]

[a]*Department of Physics, King Mongkut's University of Technology Thonburi, Bangkok, 10140, Thailand*
[b]*Western Digital Thailand Co.,Ltd., Ayutthaya, 13160, Thailand*
[c]*Thailand Center of Excellence in Physics, CHE, Ministry of Education, Bangkok 10400, Thailand*

Elsevier use only: Received 30 September 2011; Revised 10 November 2011; Accepted 25 November 2011.

Abstract

The silicon nitride/diamond-like carbon composites were fabricated using co-deposition sources. The RF magnetron was used to deposit silicon nitride simultaneously with cathodic arc deposition of carbon. The condition of RF magnetron sputtering for silicon nitride was fixed at 0.6mTorr, RF power 200 watts and 100 watts to maintain deposition rate of silicon nitride. The arc current was conditionally manipulated in this study to vary carbon deposition rate, resulting a change in composite ratio between two materials. Raman characterization and mechanical properties such as film stress and hardness were discussed as a function of deposition rate ratio. It was found that the variation of film stress follows carbon deposition rate. The Raman spectra show that the G-peak position shift to the lower wavenumber while decreasing arc current and deposition rate of carbon.

Keywords: silicon nitride; diamond like carbon; composite film; Raman spectroscopy

1. Introduction

Diamond-like carbon films have been widely used as protective overcoats for various applications such as tools, moulds, automotive parts, micro-electromechanical devices (MEMs) and magnetic storage

* Corresponding author. Tel.: +662-872-5253; fax: +662-872-5254.
E-mail address: phuwanai_b@hotmail.com.

doi:10.1016/j.proeng.2012.02.031

disk due to their exclusive properties including high hardness, smoothness of surface, low friction, good wear resistance, good adhesion, chemical inertness to acid and alkalis, and lack of magnetic response [1] as well as the ability to deposit the coating at low temperatures to maintain the magnetic properties of the magnetic material in proper condition.

In hard disk drive applications, to archive high recording density 1 Tb/in^2, it is imperative that the magnetic recording head be very close to the medium. In addition, spacing between magnetic recording head and media is the order of 10 nm is used in today's disk drives [2] and require more lower down to 6.5nm in the near future [3, 4].Thus, the reduction of head overcoat thickness is one of key however it can lead to an increase in the atomic channels or pinhole that could degrade the anti-corrosion properties and durability of protective overcoat film. The filter cathodic arc (FCA), energetic deposition process [5] has been employed in slider overcoat process of hard disk drive manufacturing since this technique produces high kinetic energy of carbon species (usually about 30-100 eV) [6] that can allow its penetration into existing film and fill in pinholes as well as forms a high-density film structure.

The modification of diamond like carbon films is one of research areas which have been studied and developed to change and improve their properties. Such as incorporate with nitrogen gas during deposition results the change in mechanical properties such as hardness, elasticity, scratch resistance and wear rate [7, 8]. Some researcher have studied and compared mechanical properties of pure DLC films and those composite DLC prepared by pulse laser deposition, which containing various types of dopants such as copper, titanium or silicon [9].

In this work, the composite DLC films were deposited using filter cathodic arc of carbon, which incorporates deposition of silicon nitride material using RF magnetron source simultaneously**.** The films properties were studied and evaluated. The 514nm visible Raman spectroscopy was used to characterize and then results were correlated with mechanical properties such as film stress and hardness.

2. Experimental details

The configuration of the system used for these experiments of composite diamond like carbon consists of two deposition sources: filter cathodic arc of carbon and RF magnetron of silicon nitride (Fig. 1).

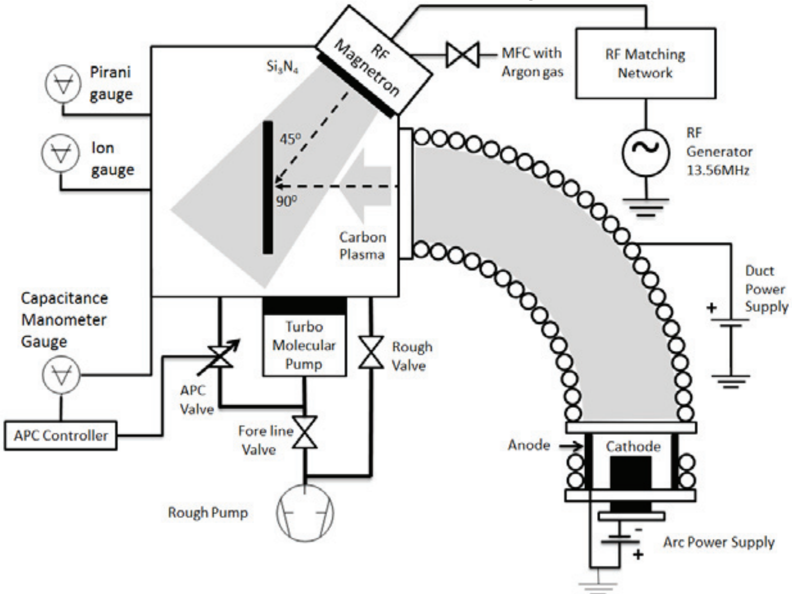


Fig. 1. Schematic of the experimental system, including vacuum components and deposition sources

The RF Magnetron sputter source equip with 6″ silicon nitride sputter target as cathode. The filter cathodic arc (FCA) carbon source with double bend magnetic solenoid filter was used as DLC deposition source. The substrate holder was floating potential. It has features of tilt and rotation capabilities. The deposition angle for silicon nitride was set as 45 degree while this angle was normal to the carbon plasma direction. The rotation was set as 15 rpm. The base pressure of the system prior to deposition was less than $5x10^{-7}$ Torr. The process pressure is able to controlled by automate pressure control (APC) with argon mass flow controller. The gas flow and pressure can be set in software, and then pressure is measured by capacitance manometer gauge and feed back to APC controller. The percentage of valve position is adjusted to archived pressure set point.

The experiments started from individual deposition rate determination. The DLC films were deposited on silicon (100) substrate from filter cathodic arc of carbon in normal direction to sample surface. The cathodic arc discharge occurs between anode and cathode graphite which ignited by the mechanical striker. The formation of cathode spots is a fundamental characteristic of the vacuum arc discharge, which moves across the surface of the cathode randomly. The plasma expands from the cathode spots into the vacuum and, in double bend electromagnetic filter duct with a copper coil wound outside and electrically isolated from the rest of the system and potential control by duct bias dc power supply (15 V). The plasma will be confined and guided by the curvilinear magnetic field that allows no straight line path between cathode arc source and the substrate and prevents neutral particles reaching substrate. The processes pressure was controlled at 0.6 mTorr by flowing with argon gas 3 sccm. The arc current was varied in the range of 20,40,60,80 and 100A, deposition time is 900 sec for each arc current setting. The Si_3N_4 deposition rate as a function of RF power was determined. The RF magnetron source consisting of 6″ diameter 99.95% Si_3N_4 target material mounted to the cathode connected with RF matchine network then connected to RF generator. The matching network consists of resistor, inductor and variable capacitor network in order to match impedance between load and source for maximum power transfer and reduction of reflected power. The process pressure was controled at 0.6 mTorr, depositon time 900 sec. and RF power was varied between 100,150,200,250,300 watts. The deposition angle was 45 degree to the substrate. The deposition rates of all samples were measured by Park Systems atomic force microscope (AFM).

The composite DLC films were deposited on silicon (100) substrate. The carbon plasma from cathodic arc of carbon was incorporated with Si_3N_4 from RF magnetron source. The condition of RF magnetron sputtering for silicon nitride was fixed at 0.6mTorr, RF power 200 watts and 100 watts to maintain deposition rate of silicon nitride in two levels. The arc current was conditionally manipulated for cathodic arc of carbon source to vary carbon deposition rate, resulting a change in concentration between two materials. The deposition rates of composite films were determined by using constant deposition time 900 seconds then thickness were measured by Park Systems atomic force microscope (AFM). The deposition rates of composite DLC in various conditions were used to calculate deposition time for 50nm films on 5 inches round silicon wafer for mechanical properties characterization. The film stress was determined by means of measuring the radius of curvature of the bare silicon substrates (R_0) and substrate after film deposition (R). The determination of stress σ of thin film with thickness t_c was given by Stoney's equation: [10].

$$\sigma = [E_s/6(1-\upsilon_s)][\,t_s^2/t_c][1/R - 1/R_0] \tag{1}$$

Where, E_s, υ_s, and t_s are the Young's modulus, Poisson ratio, and thickness of the substrate. R and R_0 are the radii of curvature of the film–substrate composite and bare substrate.

The hardness of composite DLC film was measured by nanoindentation (Hysitron Triboindentor) using cube corner tip probe 45 nm radius of curvature. The hardness is defined as the indentation load divided by projection contact area of the indentation [11].

The characterization of microstructure was performed using 514nm Ar^+ visible Raman spectroscopy (Renishaw Invia-Reflex) in back scattering geometry. The laser was focus trough 50X objective lens. The laser power at the sample was approximately 4mW. The scan range was from 1150 to 1850 cm^{-1}.The total acquisition time for each spectrum was 20 seconds. The raw spectra were fitted using two Gaussian peak as G (Graphitic) peak and D (Disorder) peak [12].

3. Results and discussion

3.1. Individual Si_3N_4 deposition rate as a function of RF Power, diamond-like carbon deposition rate as a function of arc current

The results of individual deposition rate at proces pressure condition 0.6mTorr with 3sccm argon flow rate were shown in Fig. 2 The deposition rate of Si_3N_4 increased with linear relation to RF discharge power. This affect increasing ionizaion of argon gas near cathode target. Thus, the number of argon ion bombard Si_3N_4 target were increased. In cathodic arc source, the deposition rate of carbon trend to increase with higher arc current. There were reported from previous researcher that a higer arc current affect ion density and ion saturation current increases linearly with the arc current up to 100A results in increased carbon ion gereration entering the filtering duct [13].

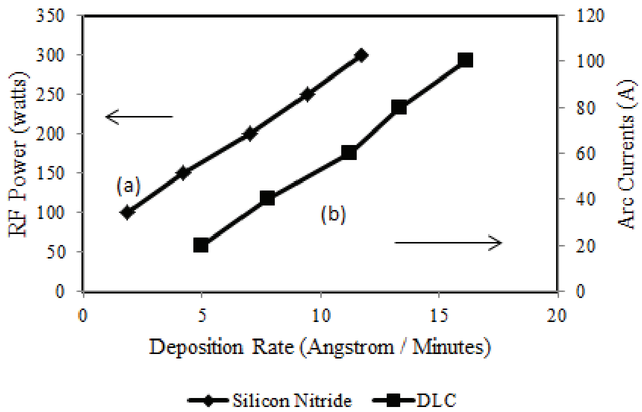


Fig. 2. (a) Si_3N_4 deposition rate as a function of RF discharge power and (b) carbon deposition rate as a function of arc current

3.2. Condition of the mix for deposition of composite DLC

The RF power 100 watts and 200 watts were selected to be maintained while the arc current was conditionally manipulated for cathodic arc of carbon source to vary carbon deposition rate, resulting a change in concentration of the mix between two materials. The estimated linear equation of carbon deposition rate in Fig. 2 was used to calculate conditions of arc current used in this experiment. The conditions of the mix for deposition of composite DLC were shown in Table 1.

The deposition rate of the composite DLC in various conditions was shown in Fig. 3. The deposition rate was affected by arc current due to carbon arc plasmas have more energetic and higher kinetic energy than Si_3N_4 which generate from RF magnetron source. The higher arc current produces more number of carbon ions entering to the substrate.

Table 1. Arc currents condition for composite DLC film

RF Power (watts)	Si_3N_4 dep. rate (Å/minute)	Ratio of dep. Rate Si_3N_4:C	Carbon dep. Rate (Å/minute)	Arc current (A) (Calculated.)
200	7.028	Pure Si_3N_4		0
200	7.028	1:0.75	5.271	21.3
200	7.028	1:1	7.028	33.8
200	7.028	1:2	14.056	84.1
100	1.873	1:3	5.620	23.8
100	1.873	1:5	9.367	50.6
100	1.873	1:8	14.986	90.8
0	0	Pure C		75.0

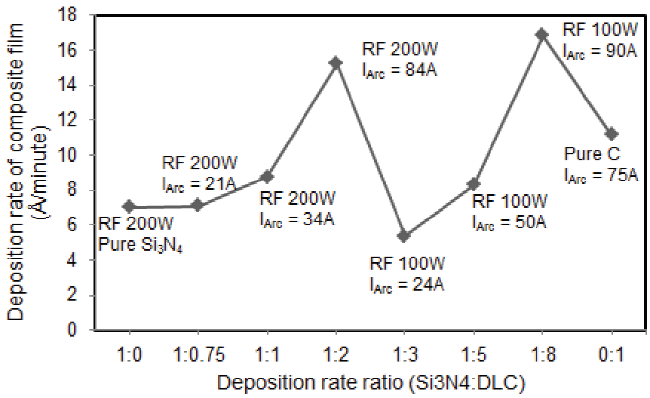


Fig. 3. Deposition rate of the composite DLC in various conditions

3.3. Raman characterization and mechanical properties

The visible Raman is more sensitive to sp^2 sites, as visible photons preferentially excite their π states [14]. These spectra can be deconvoluted into two Gaussian peaks: the G (graphitic) peak centered at approximate 1560 cm^{-1} due to graphitic E_{2g} vibration mode. It is relative motion of bond stretching of all pairs of sp^2 atoms in both rings and chains. The D (disorder) peak is due to the A_{1g} breathing modes of sp^2 atom in rings. The D peak is not found in perfect graphite [15].The qualitative trend of Raman spectra of composite DLC films on silicon substrates deposited at difference condition (deposition rate ratio between two materials) are shown in Fig. 4. The increase number of deposition rate for DLC in ratio (Si_3N_4: DLC) represent decrease of Si_3N_4 concentration in DLC films. The spectra have been displayed vertically for clarify, the results show G-Peak position shift to the lower wave number while increasing Si_3N_4 concentration (decrease DLC deposition rate). The shift in G-peak position can be interpreted that was an effect of cluster size reduction due to the interstitial of Si_3N_4 in DLC structure. The more incorporation of Si_3N_4 in the composite DLC films cause an opening up of the sp^2 ring and decrease sp^2 cluster size. Thus, the G-peak position shift to lower frequency when cluster size of sp^2 decrease [14].

The mechanical properties (stress and hardness) are shown in Fig. 5(a). Both stress and hardness are follows the same trend and decrease with more concentration of Si_3N_4 in the composite film. The incorporate of Si_3N_4 in DLC lead to reduction in sp^2 clusters. Also there are contribution of the Si_3N_4 mechanical properties which this material has lower stress and hardness compare to DLC. Thus, effects were found on both hardness and stress of the composite film reduced with increase concentration of Si_3N_4. The correlation between G peak position of the composite film and stress was shown in Fig. 5(b) the G-peak position shift in lower frequency while reduction in film stress. Thus, this result can support above that shift in G-peak position is due to cluster size effect from the interstitial of Si_3N_4 in DLC.

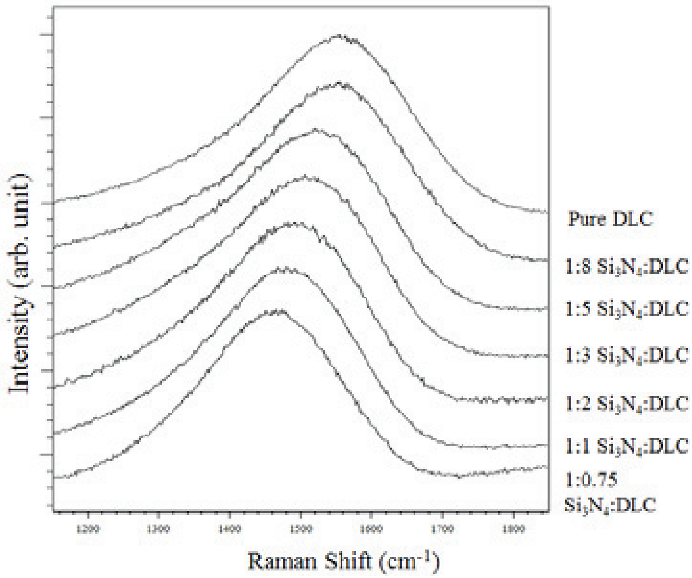
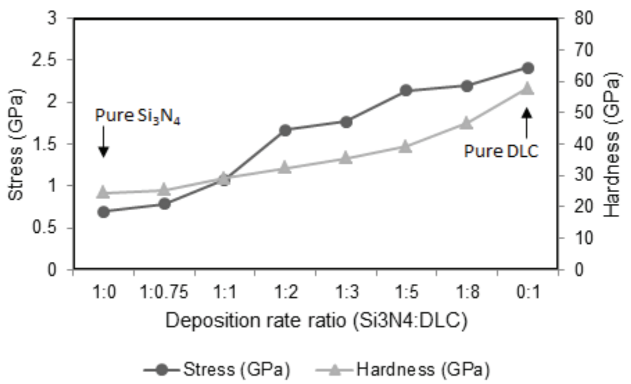
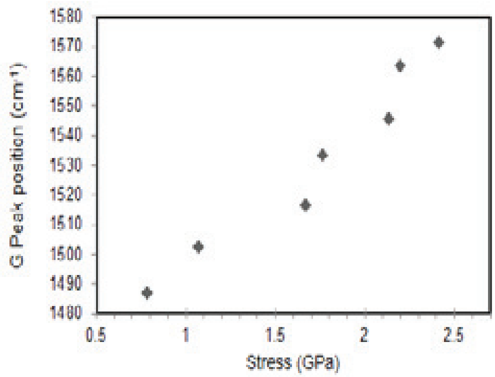


Fig. 4. The qualitative trend of 514nm Raman spectra of composite DLC films on silicon substrates deposited at difference condition (deposition rate ratio between two materials Si_3N_4:DLC)



(a)



(b)

Fig. 5. (a) Stress and hardness variation in difference deposition rate ratio (Si_3N_4:DLC) and (b) the G- peak position corelate to mechanical property (stress) of the composite Si_3N_4:DLC films

4. Conclusion

In summary, we studied the properties effect from the mix ratio between silicon nitride and DLC. The Raman spectra show G peak position shift in lower frequency while increase of Si_3N_4 concentration lead to reduction of sp^2 carbon cluster size because incorporation of Si_3N_4 cause an opening up of the sp^2 ring and decrease sp^2 cluster size. The effect can be seen in mechanical properties. The contributions of the Si_3N_4 mechanical properties which this material has lower stress and hardness compare to DLC properties. Thus the effective stress and hardness become lower while increase a concentration of Si_3N_4.

Acknowledgements

This work was supported by Western Digital Thailand and the Department of Physics, Faculty of Science. King Mongkut's University of Technology. Thonburi (KMUTT)

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